

ELECTROTHERMAL DESORPTION OF CWA SIMULANTS FROM ACTIVATED CARBON CLOTH

Patrick D. Sullivan, Joseph D. Wander, and Kolin C. Newsome

United States Air Force Research Laboratory

Tyndall AFB, Florida 32403 USA

ABSTRACT

The use of activated carbon fabrics (ACFs) that are desorbed electrothermally, also known as the Joule effect, is explored as a potential method to create a regenerating chemical warfare agent (CWA) filter. Electrical resistance vs. temperature measurements are presented for Kynol-based ACF and compared with results for ACFs produced from other substrates. Adsorption and desorption results for dimethylmethylphosphonate (DMMP) demonstrate that organophosphate compounds can be effectively desorbed from ACF. Chloroethane and propane are used to simulate the behavior of low-molecular-weight CWAs. Results for these more weakly adsorbed simulants indicate that a system that could indefinitely reject HCN without impregnants may be feasible. Planned efforts to advance this technology by both experimentation and modeling are discussed.

INTRODUCTION

The threat of chemical warfare agents to U.S. military operations at home and abroad highlights the need for improved filter protection from chemical weapons. Toxic industrial materials (TIMs) can also be used by terrorists as a low-technology alternative to military chemical weapons. Current collective protection filters require frequent replacement of the filter elements, as they can become saturated through the adsorption of non-target compounds, such as gasoline or diesel vapors and vegetation emissions. These filter change-outs are costly and add significant logistic burden. Because there is no existing indicator of remaining carbon filter life, uncertainty can cause premature change-outs. A regenerative filter system needs no replacement of the adsorptive element and could provide continuous protection during a sustained attack.

In an effort to assess the feasibility of current regenerative filter technologies, the Joint Service Chemical and Biological Defense Program has funded a research project entitled: "Advanced Regenerative Filtration Maturation for Collective Protection Applications." The advanced regenerative filtration project has been examining thermal, pressure, and electrical swing methods to regenerate adsorption-based filter systems for the removal of CWAs. Some of the electrical swing adsorption (ESA) portion of the effort is being conducted at AFRL/MLQ. AFRL is adapting a technology developed at University of Illinois (<http://www.fuentek.com/technologies/VaPRRS.htm>)[1] known as VaPRRS™, for the capture and recovery of industrial solvent vapors to also be effective for CWAs.

Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE 16 NOV 2004	2. REPORT TYPE N/A	3. DATES COVERED -		
4. TITLE AND SUBTITLE Electrothermal Desorption Of Cwa Simulants From Activated Carbon Cloth			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) United States Air Force Research Laboratory Tyndall AFB, Florida 32403 USA			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited				
13. SUPPLEMENTARY NOTES See also ADM001849, 2004 Scientific Conference on Chemical and Biological Defense Research. Held in Hunt Valley, Maryland on 15-17 November 2004 . , The original document contains color images.				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF: a. REPORT unclassified			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 11
b. ABSTRACT unclassified				
c. THIS PAGE unclassified				

Generally, CWAs are either heavier or lighter than the industrial solvents effectively treated by VaPRRS™, so the AFRL effort is looking at whether the heavier CWAs (organophosphates) can effectively be desorbed from activated carbon fiber cloth (ACFC), and also seeking to determine whether the unimpregnated carbon fabric can be configured to indefinitely reject low-molecular-weight CWAs.

The strategy for providing effective and practical regenerative filtration by ESA is based on two concepts. First, a high-performance ACFC is used to improve both adsorption capacity and adsorption dynamics over conventional adsorbents. AFRL is using an ACFC derived from a phenolic resin [2], ACC-5092-20, which is manufactured in Japan and imported by American Kynol, Inc. An exhaustive survey of all commercially available activated carbon fabrics indicated that the kynol-based ACFCs generally have the best adsorption capacity [3]. The Kynol-based ACFCs also have good performance with respect to tensile strength and friability, making them practical for implementation in a military environment where vibration will be inherent. The individual fibers of the ACC-5092-20 are $12.3 \mu\text{m} \pm 1 \mu\text{m}$ in diameter [3]. This small fiber diameter results in high external surface area, with better access to the micropore structures, which can result in twice faster adsorption dynamics than for granular activated carbon (GAC) [4]. The equilibrium adsorption capacity of ACFC can be as high as 250% of the adsorption capacity of commercial GACs [5]. ACFCs also have large surface areas, which range from $1,000 \text{ m}^2/\text{g}$ to $2,400 \text{ m}^2/\text{g}$, a typical value being $1,800 \text{ m}^2/\text{g}$ [6], [3].

The large adsorption capacities of ACFC are partially explained by its pores' existing primarily as micropores (~93%), with large micropore volumes (*e.g.*, $0.71 \text{ cm}^3/\text{g}$), and its narrow pore size distribution ([7], [8], [9]). Additional comparisons of the physical properties of an ACFC and a GAC are given in Table 1.

TABLE 1. Comparison of physical properties of an ACFC and a GAC
[from Ramirez, 2003 #679].

Adsorbent	N ₂ -BET Surface Area (m ² /g)	Total Pore Volume ^a (cm ³ /g)	N ₂ -BET Micropore Volume (cm ³ /g)	Avg. Pore Width (Å)
ACFC-5092-20 ^b	1604	0.803	0.746	7.4
Calgon BPL ^c	965	0.615	0.522	25.5

^a Single point pore volume of pores at $P/P_o = 0.98$

^b [3]

^c [10]

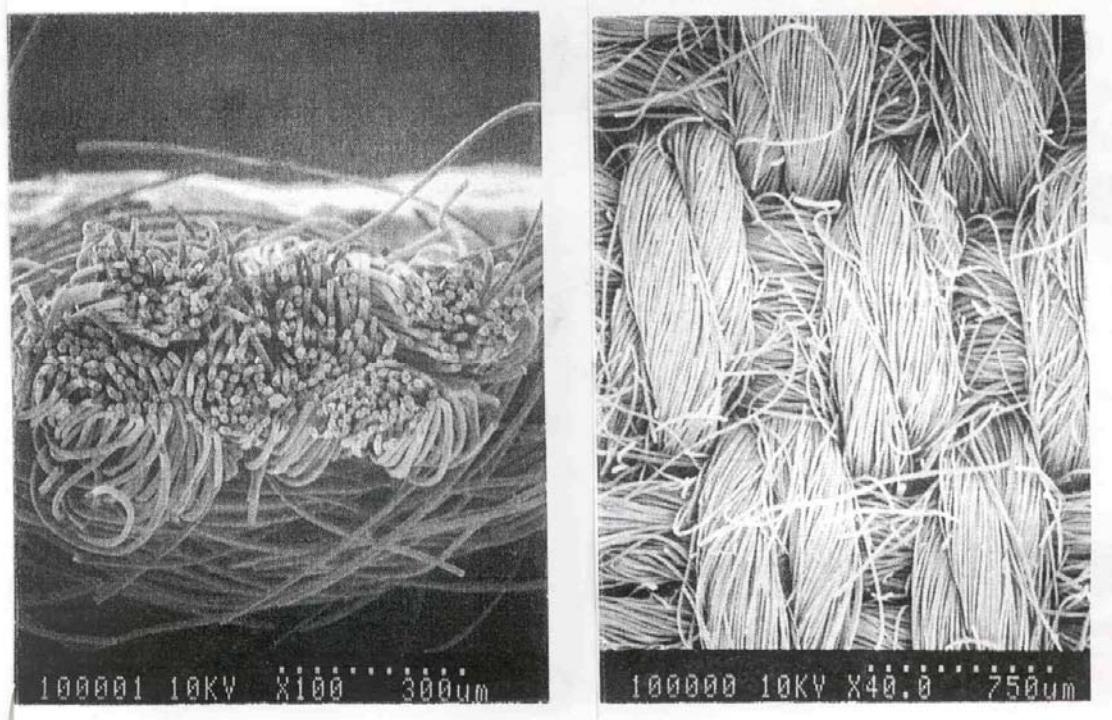


Figure 1. The structure of the ACFC ACC-5092-20[11].

The second concept that should enable ESA to be an effective technology for regenerative filtration is that heating the adsorbent directly allows more energy efficient operation and more rapid cycling. The ESA is inherently more energy efficient than conventional regeneration processes has been verified by modeling [12].

Electrical conductivity is a function of temperature. For typical conductors, the electrical resistance increases with temperature, and follows a linear relationship. Electrical resistivity of a conductor ($\rho(T)$) changes with increasing temperature as described by:

$$\rho(T) = \rho_R (1 + \alpha(T - T_R)) \quad (1)$$

where ρ_R is the resistivity of the material at T_R and α is the thermal resistivity factor of the material. Semiconductors have an electrical resistance that decreases with increasing temperature. The electrical resistance of an individual pitch-based activated carbon fiber [13] and the electrical resistances of bulk ACFCs have been reported [14], [15]. The electrical resistance of the ACFC throughout the regeneration phase is an important design parameter required for the construction of ESA devices. Previous efforts to characterize the relationship between temperature and resistivity for ACFCs have used both Eqn 1 [14], [15], [9] and an exponential relationship [16]. In an effort to clarify the relationship between temperature and resistivity for ACFC, new experimental data are presented herein.

The capability of an ESA system to provide effective regenerative filtration of CWAs is explored by challenging a system to low-molecular-weight CWA simulants.

EXPERIMENTAL APPARATUS AND METHODOLOGY

1. ELECTRICAL RESISTIVITY

The electrical resistivity tests were performed with the same adsorber used for the adsorption/desorption tests. The cylindrical portion of the adsorption vessel was made of Pyrex, with an outer diameter of 75 mm and a wall thickness of 4 mm. The vessel contained 37.45 g of ACFC (American Kynol Inc., type ACC-5092-20). The ACFC was rolled into a hollow cylinder with an inner diameter of 19 mm and an approximate outer diameter of 31.75 mm. There are 16 layers of ACFC in the annular filter element. Electrical contacts were made to the 19-mm stainless steel tubes penetrating both ends of the adsorber.

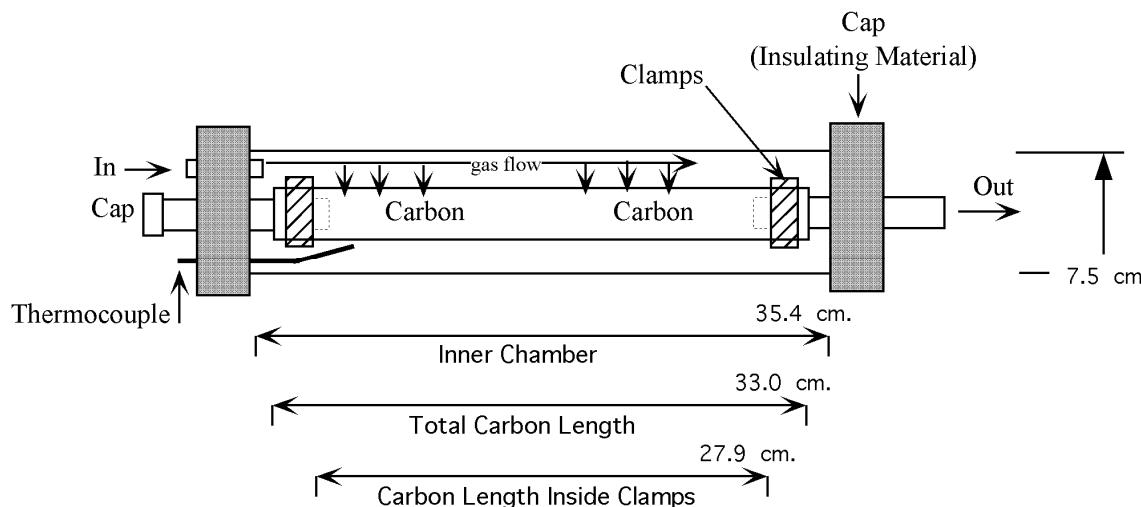


Figure 2. Adsorber used for both electrical resistivity and adsorption/desorption studies.

Power was supplied by a common laboratory power supply (Variac, Model 3PN1010). To eliminate interferences from the power supply, the ACFC was heated and then the power system disconnected. The temperature and resistance were measured as the ACFC cooled. The temperature was measured by a thermocouple (Omega Inc., Type K) in contact with the ACFC surface and logged through a distributed control system (Fieldpoint™ TC120, Fieldpoint™ F1001 and Lookout™ v.4 software). The resistances were measured with a digital multimeter (Fluke 189) and logged by hand.

2. ADSORPTION/DESORPTION

The experimental system used during adsorption and desorption tests consisted of a gas generation unit, the adsorption vessel, a direct electrical heating power supply, and a gas detection unit. For experiments with DMMP, the gas generation unit used air as the carrier gas, metered with a mass flow controller (Omega, model FMA14P4) and a set of bubblers for volatilization. For low-molecular-weight simulants, the bubblers were replaced with a standardized gas cylinder upstream of the MFC.

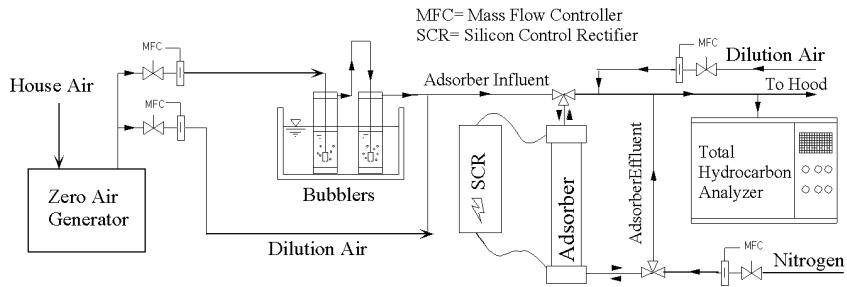


Figure 3. Schematic of system used to produce adsorption isotherms.

Thermocouples (Omega Inc., Type K) were positioned on the outer surfaces of the ACFC cartridge to monitor the temperature of the adsorbent. The thermocouples were ungrounded and electrically isolated with an electrically protected thermocouple module (Fieldpoint, Model TC-120) because the thermocouples were in contact with the ACFC as electrical current passed through the ACFC. Total gas flow rates during these breakthrough tests were 5 sLpm. The bed was regenerated between runs by increasing the ACFC's temperature to 200°C–300°C while purging the vessel with ultrahigh-purity (UHP) N_{2(g)}. Direct electrical heating was applied to the ACFC with a power supply (Variac, 3PN1010) using alternating current. Effluent concentration of the adsorber was measured by a total hydrocarbon analyzer using flame ionization detection (THC/FID, California Analytical, Model 300-HFID).

Breakthrough curves were collected for chloroethane and propane. The adsorption capacity of the ACFC can be computed from the breakthrough curve by:

$$W = \frac{P_{tot} (MW) Q_{air}}{\rho_l m_s R T} \int_0^{t_{sat}} \left(\frac{C_{in}}{1 - C_{in}} - \frac{C_{out}}{1 - C_{out}} \right) dt \quad (2)$$

where W is the volume of adsorbed organic vapor per unit mass of adsorbent, P_{tot} is the total pressure of the inlet gas stream, MW is the molecular weight of the adsorbate, Q_{air} is the volume flow rate of carrier gas, R is the ideal gas constant, T is the absolute temperature of the inlet carrier gas, m_s is the mass of the adsorbent, ρ_l is the bulk liquid density of the adsorbate, C_{in} is the mole fraction of adsorbate in the inlet gas stream, C_{out} is the mole fraction of adsorbate in the exhaust gas stream, and t_{sat} is the time at which C_{out} has reached its final, steady-state value because the adsorbent is saturated with respect to the adsorbate.

N_{2(g)} gas purge rate during desorption was 2 sLpm. Additional dilution air was added to the desorption stream to get the effluent within the detection limit of the analyzer, which was 30,000 ppmv. The mass of desorbed adsorbate is described by

$$M_{desorb} = \frac{P (MW) Q_{N2}}{R T} \int_0^{t_{fin}} \left(\frac{C_{out}}{1 - C_{out}} \right) dt \quad (3)$$

where, Q_{N2} is the carrier gas flow rate, C_{out} is the concentration of adsorbate in the gas stream exiting the bed (mole fraction), and t_{fin} is the duration of the desorption cycle.

RESULTS AND DISCUSSION

1. ELECTRICAL RESISTIVITY

Resistances relative to the initial resistance vs. temperature are plotted for three ACFCs. All three of the ACFCs show significant nonlinear behavior. The previous published data for ACC-5092-20, which have been fitted to Eqn 1[9],[14], [15] have been over a smaller temperature range and have included fewer data points.

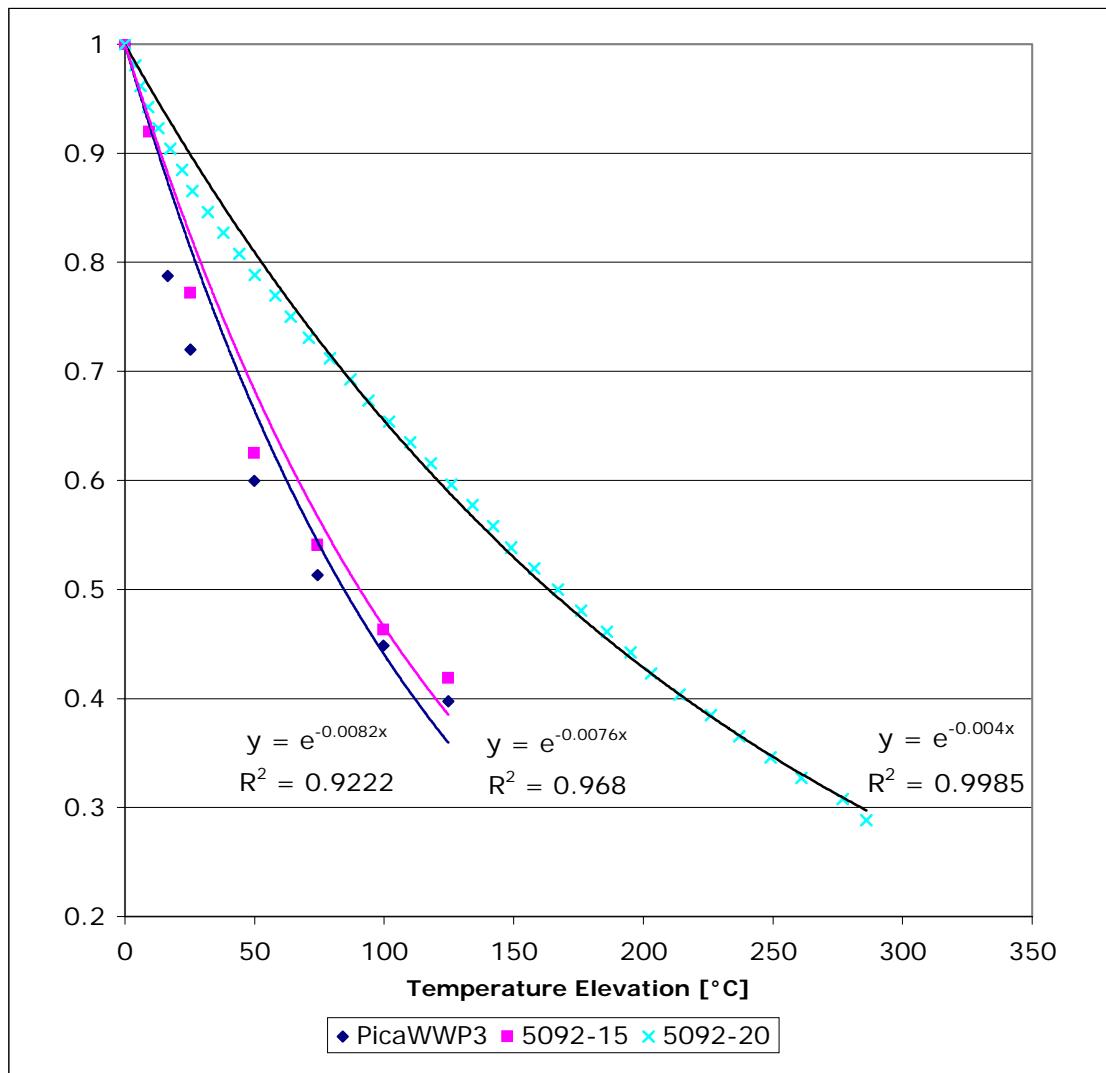


Figure 4. Electrical resistance with respect to temperature for three ACFCs. PicaWWP3 and ACC-5092-15 by K. Knaebel [17] and ACC-5092-20 by the authors.

2. ADSORPTION/DESORPTION

Closures for the mass balances were evaluated by comparing the mass adsorbed to the mass desorbed (Eqns 2 and 3, respectively). As previously mentioned, N₂ gas flow was 2 sLpm for all regeneration tests. The material balances provided closure within +5%. These closures are reasonable when considering the margin of in the flow and concentration measurements.

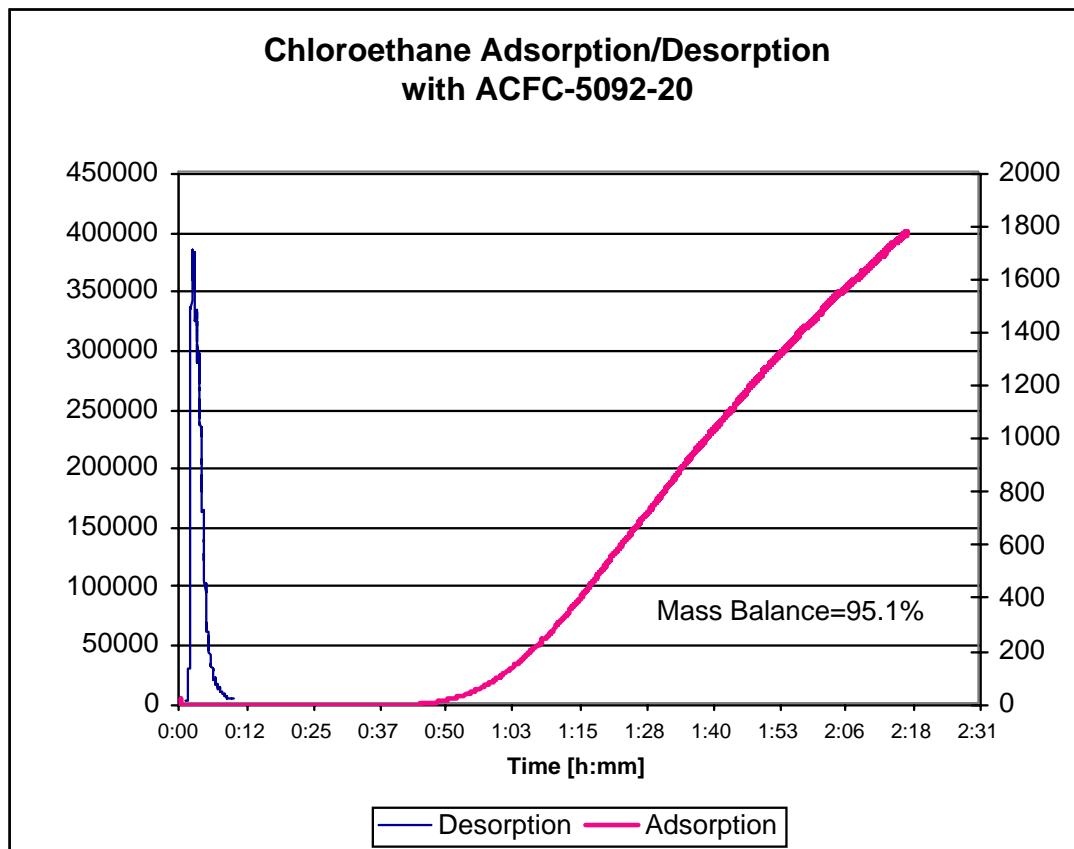


Figure 5. Adsorption and desorption of chloroethane with ACC-5092-20.

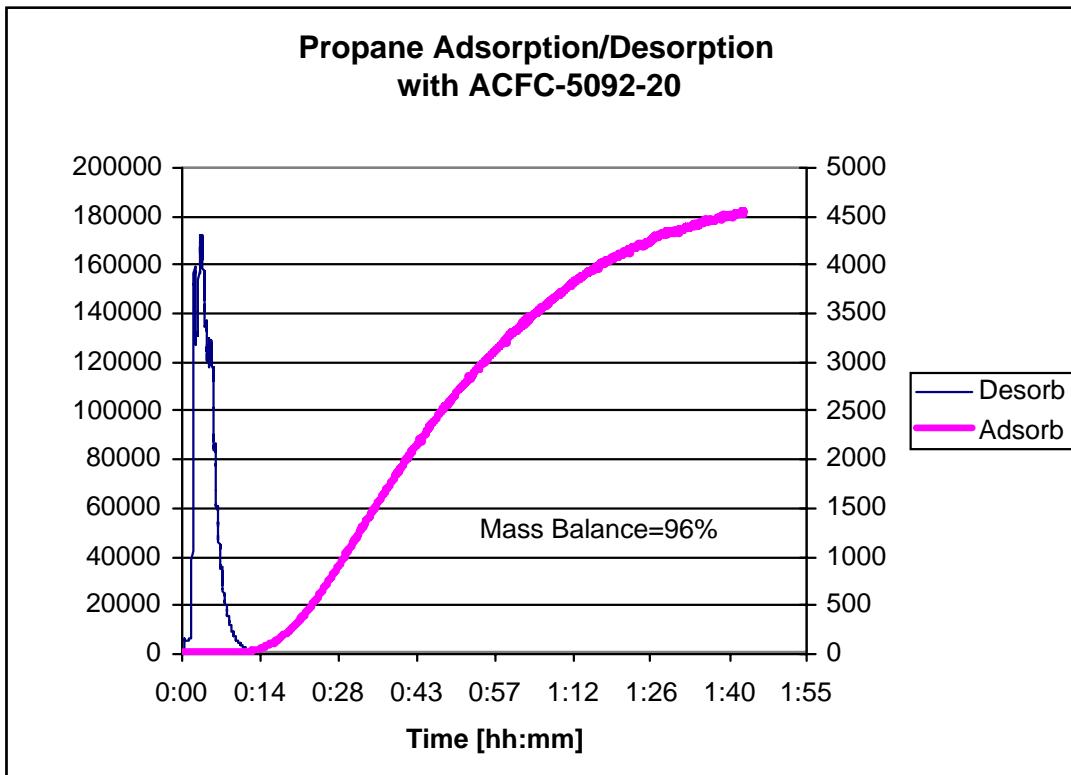


Figure 6. Adsorption and desorption of propane with ACC-5092-20.

The plot for chloroethane shows that the adsorption runtime prior to breakthrough is more than four times greater than the desorption time. The actual feed concentration of the chloroethane was 5000 ppmv, but the adsorption run was not extended to complete saturation, and the concentration plotted is not corrected for the response factor of the THC/FID. The tests were conducted with zero humidity, and so some reduction in runtime would be experienced in conditions with humidity greater than 60%. Previous tests with ACC-5092-20 and methyl ethyl ketone showed a reduction of about 40% [14], but also showed that this reduction can be halved by increasing the bed temperature slightly (5°C – 10°C) during adsorption.

The plot for propane has an adsorption runtime prior to breakthrough approximately equal to the desorption time. This is promising, in that the adsorber design used is not optimized, and therefore better performance can be expected with engineering refinement. The desorption time for chloroethane is no longer than that for propane, despite the fact that about twice the mass was desorbed. Based on the propane results, it is likely that an ESA system could be engineered to reject HCN and possibly other toxic industrial materials that are permanent gases.

3. FUTURE WORK

The current laboratory set-up cannot reject compounds with lower adsorption capacities than propane, as the adsorption and desorption cycle times are nearly equal. It may be possible to build an ESA system that can indefinitely reject HCN (and other permanent

gas TIC/TIMs), but an improved adsorber configuration is required. The limitations of the process and the best adsorber design can more efficiently be determined by modeling and simulation rather than by trial and error. The modeling of the adsorption portion of the process is similar to models already developed at Edgewood Chemical and Biological Center, Md. Desorption from an ESA system is, however, very different than desorption from conventional filter systems, so additional phenomena must be modeled to simulate filter regeneration. ESA desorption may include in-vessel condensation, depending on the vapor pressure of the adsorbate, and free convection in the annular space plays an important role in the mass and energy transport in the process. Transport in the annular space requires that computational fluid dynamics (CFD) be integrated with the model, greatly increasing its complexity.

AFRL has already begun an investigational modeling effort designed to determine feasible approaches. Output from the commercial modeling suite Femlab™ 3 is shown for a preliminary representation of the AFRL bench-scale system. The model is axisymmetric and two dimensional. From left to right, the regions represented are the air space inside the ACFC cartridge, the ACFC layer (both red), the annular space (multicolored with velocity lines), and the vessel shell (blue).

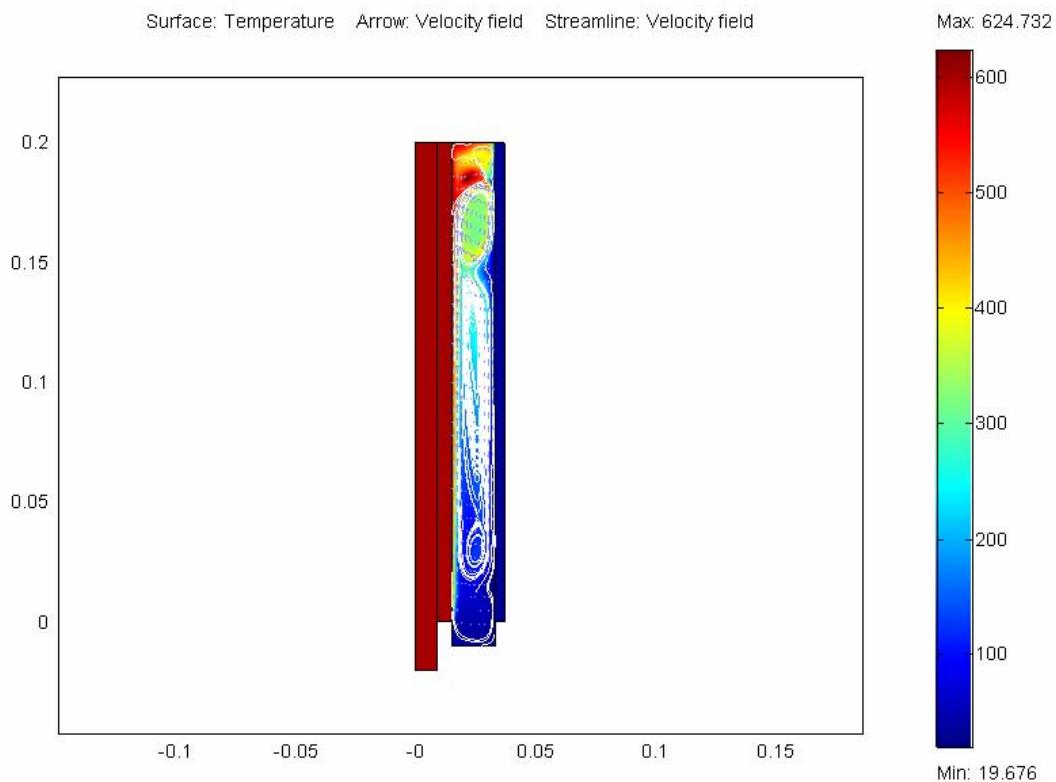


Figure 7. Two-dimensional, axisymmetric model of temperatures in AFRL bench-scale ESA system during regeneration.

Femlab™ 3, released in February 2004, is capable of solving multiple, coupled, partial differential equations. It appears to be ideally suited for modeling the complex ESA regeneration process, if the CFD portion of the code can be made to accurately represent the convective transport. AFRL proposes to use Femlab™ 3 in the research effort.

In a similar effort, the University of Illinois at Urbana–Champaign (UIUC) is also attempting to model the ESA process, except with an emphasis on industrial solvent recovery applications. UIUC is using a combination of FLUENT™ and Matlab™ to model the process. AFRL, UIUC, and University of Belgrade will be cooperating in an effort to compare and evaluate the two modeling approaches.

The computer modeling efforts should provide predictive rapid prototyping tools to assist in optimizing ESA designs. In addition, a pilot-scale prototype is planned to provide more data for scale-up and model validation.

CONCLUSIONS

The previously published data for temperature versus resistivity for ACFCs fitted to Eqn 1 has been over a smaller temperature range and has included fewer data points than the data presented here. The new data support the conclusion that the exponential form favored by Petkovska [16] more accurately describes the thermal conductivity relationship for ACFCs. Accurate information on the thermal conductivity relationship is needed for designing devices, as the power input is inversely proportional to the ACFC resistance, and the regeneration during heating by nature is a run-away process at constant potential.

An ESA system was demonstrated that has an adsorption runtime roughly equal to the desorption time when challenged with 5000 ppmv of propane. These results merit further investigation into optimizing ESA systems, as a regenerable filter that rejects all CWAs indefinitely for collective protection applications may be achievable.

REFERENCES

1. UIUC, U.of Illinois.at.U.-C., *VaPRRS™ technology for effective air quality control*, 2004, Fuentek, <http://www.fuentek.com/technologies/VaPRRS.htm>.
2. Hayes Jr., J.S., *Novoloid Fibers*, in *Kirk-Othmer: Encyclopedia of Chemical Technology*. 1981, John Wiley & Sons, Inc. p. 125–138.
3. Lo, S.-Y., *Characterization of the chemical, physical, thermal and electrical properties of a series of activated carbon fiber cloths*, in *Environmental Engineering in Civil Engineering*. 2002, University of Illinois at Urbana–Champaign: Urbana. p. 110.
4. Tsai, W.T., *et al.*, "Adsorption Properties and Breakthrough Model of 1,1-Dichloro-1-fluoroethane on Granular Activated Carbon and Activated Carbon Fiber." *Separation Science and Technology*, 2000. **35**(10): p. 1635–1650.
5. Ramirez, *et al.* "Adsorption of Organic Vapors on Tire, Coal and Phenol Derived Activated Carbons" in *Proceedings of A&WMA 94th Annual Meeting & Exhibition*. 2001. Salt Lake City, Utah: Paper #456.
6. Foster, K.L., *et al.*, "Adsorption Characteristics of Trace Volatile Organic-Compounds in Gas Streams Onto Activated Carbon-Fibers." *Chemistry of Materials*, 1992. **4**(5): p. 1068–1073.

7. Hsi, H.-C., *et al.* "Mercury vapor removal from simulated flue gases with Illinois coal-derived activated carbon (ICDAC)" in *Proceedings of A&WMA 91st Annual Meeting*. 1998. San Diego, California.
8. Sun, J., *et al.*, "Correlating N₂ and CH₄ Adsorption on Microporous Carbon Using a New Analytical Model." *Energy & Fuels*, 1998. **12**(6): 1071–1078.
9. Lordgooei, M., *Adsorption Thermodynamics and Mass Transfer of Toxic Volatile Organic Compounds in Activated-Carbon Fiber Cloth for Air Pollution Control*, in *Environmental Engineering in Civil Engineering*. 1999, University of Illinois at Urbana–Champaign: Urbana. p. 184.
10. Lehmann, C.M.B., *et al.*, "Reprocessing and Reuse of Waste Tire Rubber to Solve Air-Quality Related Problems. Energy & Fuels," 1998. **12**:1095–1099.
11. Lordgooei, M., *et al.*, "Development of an Activated Carbon Fiber Cloth Adsorption/Regeneration System to Recover and Reuse Toxic Organic Compounds," 1996, Hazardous Waste Research and Information Center: Champaign, Illinois. 206.
12. Petkovska, M. and M. Mitrovic, "One-Dimensional, Nonadiabatic, Microscopic Model of Electrothermal Desorption Process Dynamics." *Chemical Engineering Research & Design*, 1994. **72**(A6): 713–722.
13. Nakayama, A., *et al.*, "Electronic and magnetic properties of activated carbon fibers." *Bull. Chem Soc Japan*, 1996. **69**(2): 333–339.
14. Sullivan, P.D., *et al.*, "Adsorption and Electrothermal Desorption of Hazardous Organic Vapors." *J. Environmental Eng.*, 2001. **127**(3): 217–223.
15. Subrenat, A., *et al.*, "Electrical behaviour of activated carbon cloth heated by the Joule effect: desorption application." *Carbon*, 2001. **39**: 707–716.
16. Petkovska, M. and M. Mitrovic, "Dynamics of electrothermal desorption process: a heterogeneous one-dimensional macroscopic model." *J. Serb. Chem. Soc.*, 1992. **57**: 319.
17. Knaebel, K., *Unpublished Report*, 2002, SBCCOM.